EXHIBIT U

Permanence of Polymer Stabilizers in Hostile Environments

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SYNOPSIS

Additives are commonly formulated into polymers to stabilize them against thermo-oxidative and photo-oxidative degradation. However, the additives themselves undergo degradation in the polymers, especially when the polymers are placed in hostile environments. This study focuses on the degradation of additives in chemical and photo-oxidizing environments; i.e., spas and xenon arc, respectively. HPLC-UV/vis, FT-IR, and GC-MS techniques were utilized to follow the degradation chemistry of the additives. The chemistry was determined for additive degradation by spa chemicals, but the degradation chemistry of benzotriazoles remains elusive due to the insolubility of the resinous degradation products.

INTRODUCTION

Plastics are degraded during processing by both physical (shear, heat, light) and chemical (oxidizing chemicals) deteriogens. Stabilizers are usually added to polymers to scavenge or neutralize the effect of deteriogens, thus prolonging the lifetime of the plastic. Some plastics are used in especially hostile environments where they are exposed to a variety of deteriogens that cause the polymer to degrade by several differing mechanisms. Effective stabilization of plastics used in these environments requires the addition of several different types of stabilizers that work together in a synergistic manner.

Stabilizers can be classified according to the mechanism of how they protect the plastic around them. Main classes of stabilizers include: chain-breaking antioxidants such as hindered phenols (HP), hydroperoxide decomposing antioxidants such as phosphites (PP), and light stabilizers that function as UV absorbers (UVA) such as benzotriazoles and hydroxybenzophenones (HBP), or as radical scavengers such as hindered amine light stabilizers (HALS).

A key factor controlling the lifetime of plastics used in hostile environments is the permanence of the stabilizers. Most of the research in the area of stabilizer permanence has focused on physical loss mechanisms.[1] Loss by chemical degradation of the stabilizer has been observed in polyolefins.[2-6] Chakraborty and Scott[7] and Hodgeman[8] studied the degradation of HBP and UVA, respectively, by attack of peroxy radicals in solution as a model for possible reactions of UVA stabilizers with the intermediate peroxy radicals involved in thermal and photo-oxidation of polymers. In the current study we focus on chemical loss mechanisms of polymer stabilizers used in plastics placed in environments where exposure to UV radiation and strong oxidizing chemicals takes place (e.g., swimming pools).

EXPERIMENTAL

Sample Preparation

Stabilizers were premeasured and shaken in a polyethylene bag with polymer granules until the stabilizers were distributed thoroughly. The samples were then compounded on a W.E. Extruder and extruded into a tape 4 cm wide and 2 mm thick using a Brabender extruder.

HPLC Analyses

The HPLC procedure used during this study is described in detail elsewhere.[9]

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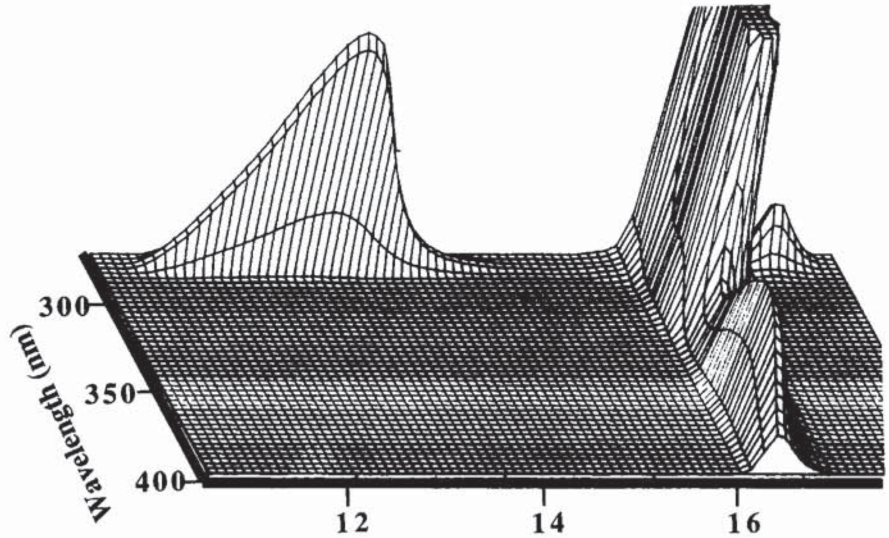
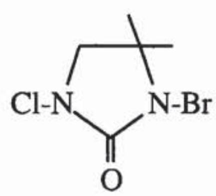


Figure 1 GPC-UV/vis chromatogram of orange swimming pool part.

Procedure for Exposure of Stabilized Plastics to Spa Water

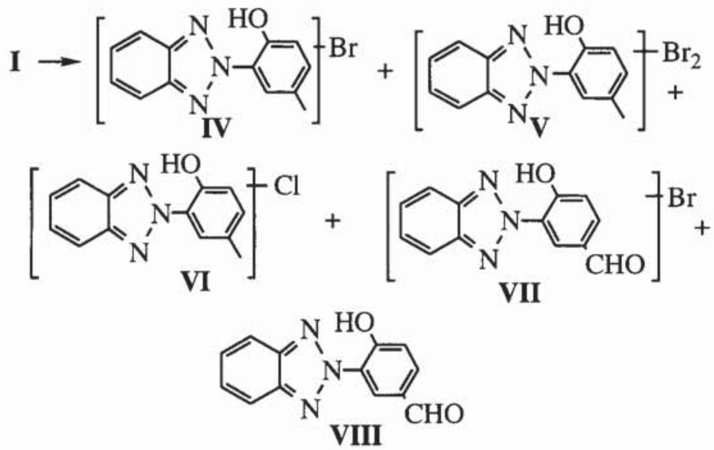
A tank equipped with a mechanical stirrer and temperature controller was filled with a spa water solution containing 20 ppm of total halogen (added as *N*-bromo, *N'*-chloro-hydantoin), 123 ppm magnesium sulfate, 84 ppm sodium bicarbonate, and 146 ppm calcium chloride dihydrate. The extruded tapes described above were cut into strips and immersed for 24 h in the spa water solution at 40°C. Any changes in the appearance of the plastic were noted.



N-bromo, N'-chloro-hydantoin

Table 1 **Discoloration Rate Upon Exposure to a Spa Chemical in Solution**

Stabilizer/Type	Color	Time
2-(2'-hydroxy-5'-methylphenyl)-benzenetriazole/UVA	yellow	1 d
2-(2'-hydroxy-3',5'-*t*-diamylphenyl)-benzenetriazole/UVA	yellow	1 d
Bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate/HALS	yellow	1 h
Bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate/HALS	none	
Octadecyl(3,5-di-tert-butyl-4-hydroxy)hydrocinnamate/HP	yellow	1 m
Bis(3,5-di-tert-butyl-4-hydroxy-hydrocinnamoyl)hydrazide/HP	brown	1 m
2,4,6-Tris(3,5-di-tert-butyl-4-hydroxybenzyl)mesitylene/HP	yellow	1 m
1,1,3-Tris(3-tert-butyl-4-hydroxy-6-methylphenyl)butane/HP	brown	1 m
Tris(3,5-dibutyl-4-hydroxybenzyl)isocyanurate/HP	green	1 m
Tris(4-nonylphenyl)phosphite/PP	brown	1 m
Tris(2,4-di-t-butylphenyl)phosphite/PP	brown	1 m



Scheme 1 Proposed degradation chemistry of a typical UVA.

Procedure for Reaction of Stabilizers with Spa Chemical

A solution was prepared consisting of 1 mmol of *N*-bromo, *N'*-chloro-hydantoin in methylene chloride that had been previously saturated with water. This solution was used to dissolve stabilizers at 0.1% by weight in glass bottles. Color changes that took place were noted after 1 min, 1 h, and 1 day. HPLC and GC/MS analyses analyses were performed on some of the solutions to determine changes in the stabilizer structure.

Xenon Arc Exposure

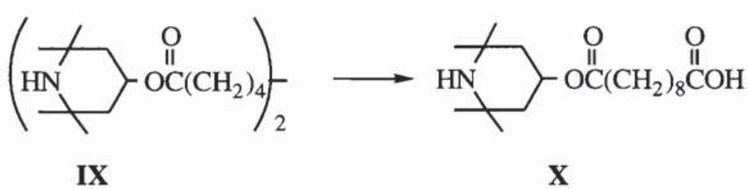
Samples were placed into an Atlas Ci65 xenon arc Weather-Ometer for accelerated weathering using ASTM D2565 conditions.

UV Absorbance Color Measurement

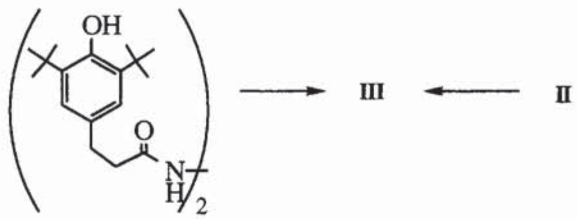
The xenon arc exposed samples were removed from the xenon arc, and the UV absorbance spectrum recorded using a Shimadzu UV/vis Spectrophotometer. The color readings were taken after each exposure using a HunterLab Ultrascan. The samples were returned to the xenon arc immediately following the measurement.

RESULTS AND DISCUSSION

We obtained a swimming pool accessory part that had turned bright orange during use. The source of the plastic used in its manufacture was unknown. ^{13}C NMR analysis of the plastic indicated that it was an acrylate rubber (ASA) modified styrene-*co*-acrylonitrile (SAN). The polymer sample was dissolved in methylene chloride, filtered to remove insoluble materials, and analyzed using GPC-UV/vis analysis to determine the location of the orange color. We have previously described in detail application of GPC-UV/vis analysis for locating chromophores in polymers.[10] In our work we have observed the formation of chromophores on chain ends,[11] randomly distributed along the polymer backbone,[12] in the high molecular weight chains, in the small molecules, and combinations of these.[13] The results of the GPC-UV/vis analysis (Fig. 1) clearly shows that the visible absorbing portion of the polymer is located in small molecules in the



Scheme 2 Proposed degradation chemistry of a typical HALS.

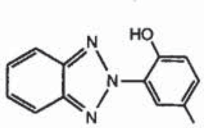


XI

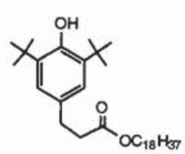
Scheme 3 Proposed degradation chemistry of typical HP.

polymer. The molecular weight of the orange-colored molecules are estimated to be 300–400, based on the calibration curve for the GPC column set.

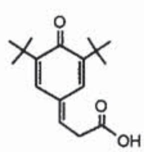
Methanol was added to precipitate the polymer from the methylene cloride solution. The orange color remained in solution supporting the GPC-UV/vis result. HPLC analysis of the solution showed the presence of 2-(2′-hydroxy-4′-methylphenyl)-benzenetriazole (UVA-1) (I) and octadecyl(3,5-di-*tert-butyl*-4-hydroxy)hydrocinnamate, a hindered phenol (HP) (II) along with several unknown compounds, some having absorbance in the visible portion (> 400 nm) of the UV-vis spectrum. GC-MS analysis of the solution showed that it contained I, a compound having the mass of I + chlorine and several oxidized and/or chlorinated phenolic compounds. The oxidized phenolic compound in highest amount gave a mass spectrum consistent with III.



UVA-1 (I)



II



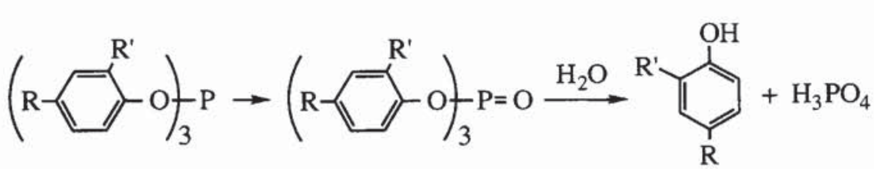
III

An investigation was conducted to see if discoloration of a plastic upon exposure to swimming pool/spa chemicals is entirely due to reactions of the stabilizers or if discoloration reactions also take place in the polymer structure itself. This was studied by preparing a plastic (ASA toughened SAN) test specimens (extruded tapes) with and without stabilizers present. The test specimens were immersed in an agitated tank containing spa water rich in halogen (20 ppm total halogen) and temperature controlled at 40°C. The appearance of the specimens was noted after 24 h exposure.

The stabilizer mixture evaluated consisted of a UVA, a HALS, and a HP. All of the test specimens containing the stabilizer mixture turned yellow-orange, while the appearance of the unstabilized specimens remained unchanged. These experiments confirm that discoloration is primarily due to interaction of stabilizers and swimming pool/spa chemicals.

To better understand the chemistry of the interaction of stabilizers and swimming pool/spa chemicals, various stabilizers were treated with a spa chemical (*N*-bromo, *N*′-chloro-hydantoin) in methylene chloride solution. Table I summarizes the visual results of this experiment.

Five of the solutions from Table I were analyzed by HPLC and GC/MS to determine the nature of stabilizer-spa chemical reactions. UVA-1 (I) was converted into five new compounds (Scheme 1) upon treatment with *N*-bromo, *N*′-chloro-hydantoin. These compounds gave mass spectral data consistent with the addition of bromine (IV and V), chlorine (VI) and/or oxidation (VII and VIII). A HALS [Bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate] (IX) was hydrolyzed (X) (Scheme 2). Treatment of two hindered phenols (II) and 1,2-Bis(3,5-di-*tert-butyl*-4-hydroxy-hydrocinnamoyl)hydrazide (XI) with *N*-bromo, *N*′-chloro-hydantoin resulted in hydrolysis and oxidation as previously observed in the orange pool accessory (Scheme 3). Although III was by far the largest product of XI degradation, nine other minor products were observed. These included III + chlorine and several oxidized and chlorinated forms of the unhydrolyzed molecule. Two phosphites



XII R=R'=t-butyl **XIV** **XV**

XIII R=C_9H_{39}, R'=H

Scheme 4 Proposed degradation chemistry of typical phosphites.

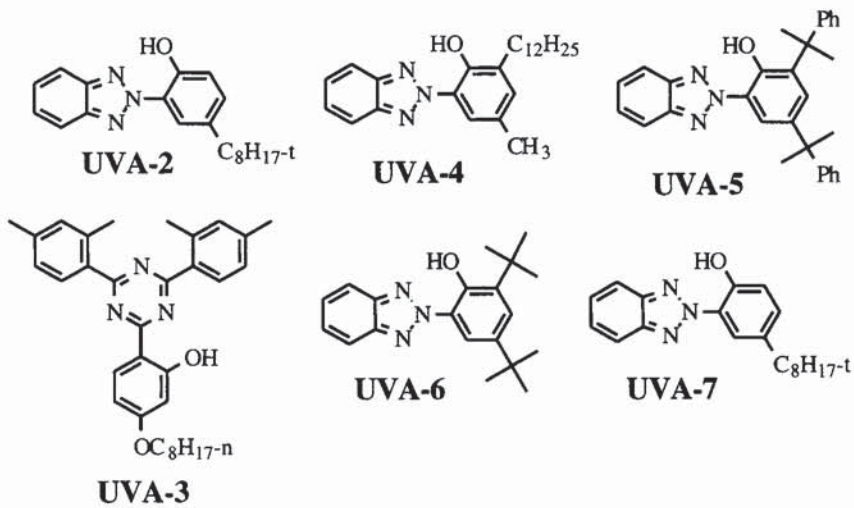


Figure 2 Structures of UVA evaluated in this study.

[tris(2,4-di-*t-butyl*phenyl)phosphite (XII) and tris(4-nonylphenyl)phosphite (XIII)] were also oxidized (XIV) and hydrolyzed (XV) upon exposure to *N*-bromo, *N'*-chloro-hydantoin (Scheme 4).

UVA are a class of stabilizers utilized heavily in plastics and coatings that will be used in environments where exposure to UV radiation is frequent. To explore the permanence of UVA under UV exposure, various UVA additives (Fig. 2) were compounded into an acrylic polymer (Rohm and Haas DR Acrylic). Extruded tape test specimens were prepared and exposed in a xenon arc. The UVA level in the plastic was measured after various exposure intervals using direct UV analysis, HPLC, and GC. All three techniques show a first order loss (Fig. 3) of the UVA additives evaluated. Exposure of the test

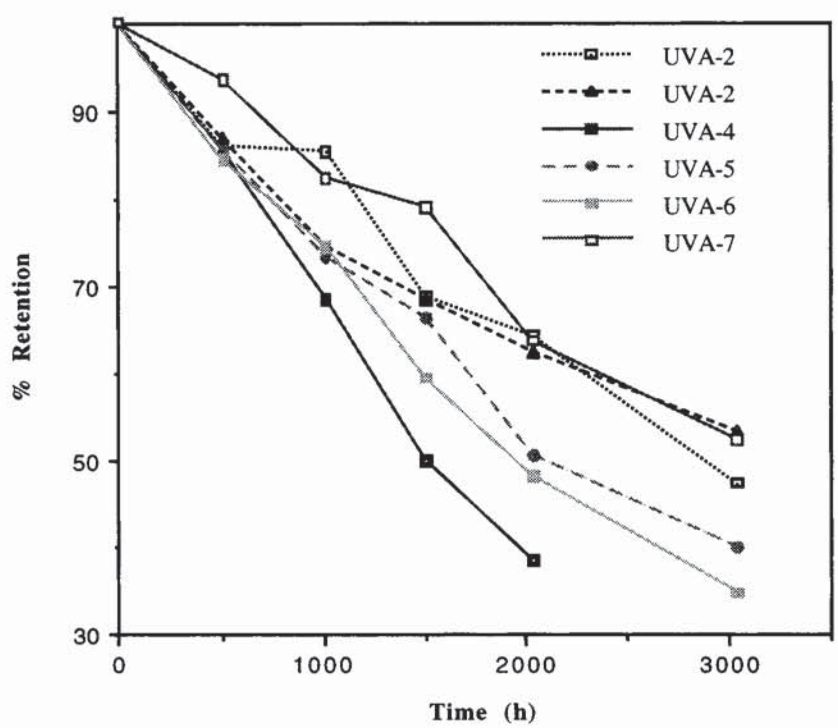


Figure 3 Loss of several UVA from DR acrylic during Irradiation in xenon arc.

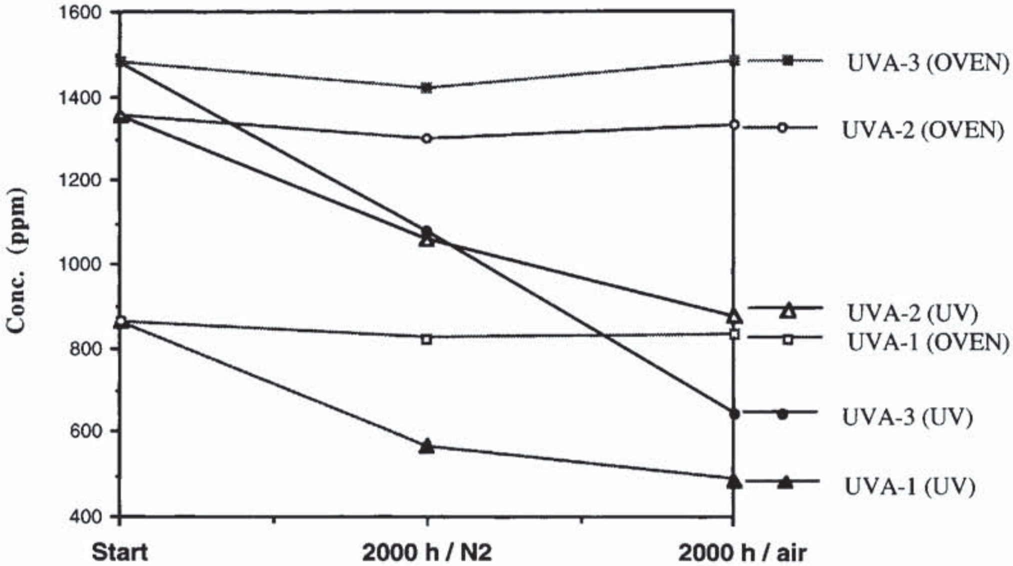


Figure 4 Loss of UVA during xenon arc and oven exposure in quartz ampoules.

specimens in an oven heated at a higher temperature (80°C) than the inside of the xenon arc, showed no loss of UVA. This indicates that the loss mechanism of UVA is not by evaporation. HPLC and GC showed no new compounds formed during the loss of UVA.

One hypothesis for UVA loss is that the diffusion and evaporation of the UVA is catalyzed by exposure to light. To test this hypothesis, test specimens were sealed inside quartz ampoules. Each specimen was sealed in four ampoules. Two ampoules were filled with nitrogen and two filled with air. One ampoule filled with each gas was placed in a xenon arc and one filled with each gas placed inside an oven at 80°C for 2000 h. The level of UVA in the acrylic test specimens before and after UV and oven exposure for 2000 h in the ampoules is shown in Figure 4.

After the 2000 h xenon arc exposure, the test specimens were removed from the ampoules and the ampoules washed with 1 cc of isooctane. The isooctane was analyzed by GC and HPLC for the presence of trace levels of UVA and other compounds. No UVA or other nitrogen containing organic compounds were found.

To aid in the identification of chemical degradation pathways of UVA during photolysis, UVA-1

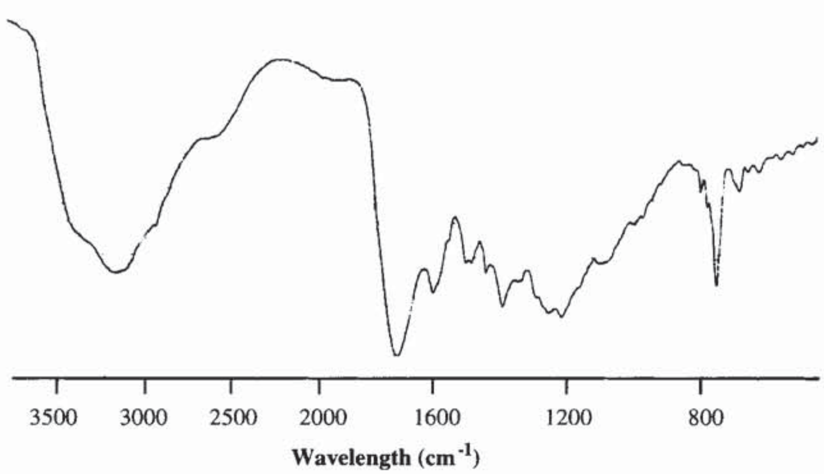
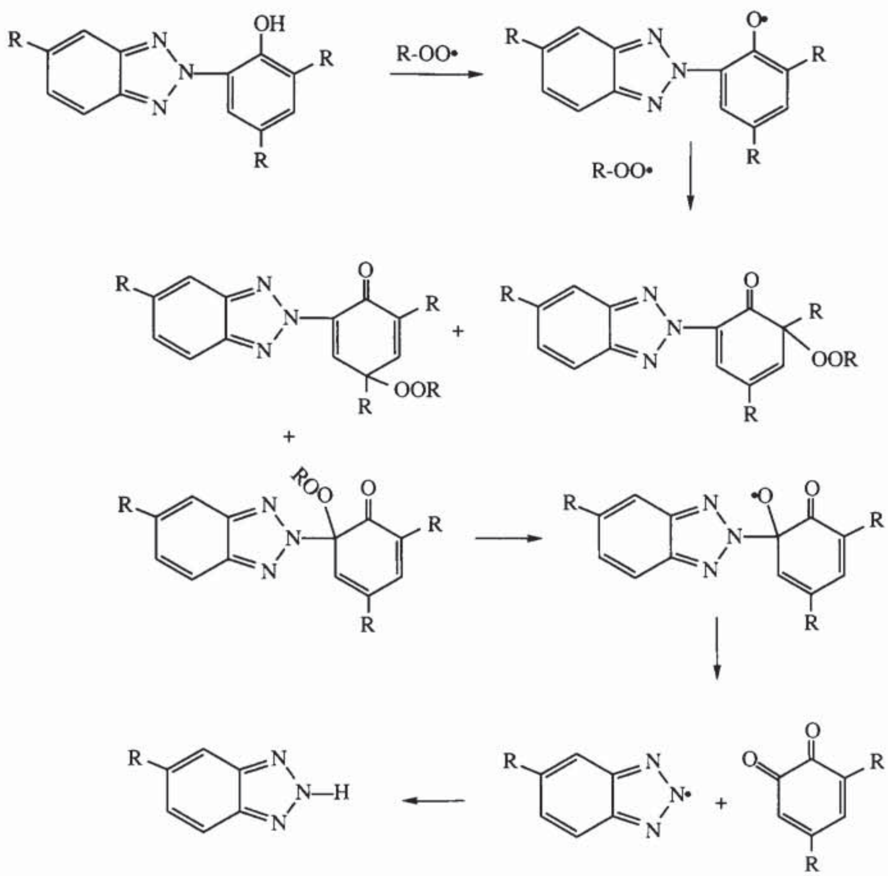


Figure 5 FT-IR spectrum of the degradation product of UVA-1 in benzene solution after 4000 h of exposure in a xenon arc.



Scheme 5 UVA degradation mechanism proposed by Hodgeman.[8]

was dissolved in benzene at a concentration of 0.011 g/L. Again, loss of UVA-1 followed first-order kinetics, but the synchronous formation of new molecules was not observed when analyzing the benzene solution using HPLC and GC. After 4000 h, a brown residue was noticed on the side of the vial. The benzene was decanted from the vial and tetrahydrofuran added. However, the residue remained insoluble. The residue was scraped from the side of the vial and analyzed using FT-IR. However, its spectrum was not very informative (Fig. 5).

The conversion of UVA-1 to an insoluble resinous material explains why its decomposition products are not observed upon irradiation of UVA stabilized plastics. The UVA is being degraded to an insoluble resinous material that cannot be separated from the plastic for analysis. Hodgeman[8] suggest that the mechanism of UVA degradation involves hydrogen abstraction from the phenol resulting in oxidation of the phenolic ring to quinone structures followed by addition of peroxy radicals to the quinone ring. Furthermore, he proposed ultimate sission of the UVA molecule between the phenolic and benzene-triazole rings (Scheme 5).

Our results suggest that the UVA-1 distruction mechanism involves oxidation, but not the scission processes proposed by Hodgeman. Instead, we believe that radical coupling reactions take place resulting in formation of a resinous material.

CONCLUSIONS

Spas and swimming pools contain strong chemical oxidizers and represent a very hostile environment for organic compounds. Plastics and coatings being used in this environment must be stabilized to protect them against oxidative degradation. Exposure of the common classes of polymer stabilizers to a chemical typically used in spas, resulted in hydrolysis of ester and amide linkages, and oxidation and halogenation of phenolic moieties in the stabilizers. Stabilizer types that were found to discolor the fast-

est upon exposure to the spa chemical were hindered phenols and phosphites.

The mechanism of loss of UVA during UV exposure is not known at this time. The UVA permanence during oven exposure, accompanied by the loss upon UV exposure under nitrogen and even greater loss under air, indicate that the UVA are chemically degrading. However, unlike the spa chemical experiments, we have not yet been able to identify the products of chemical degradation because they are converted to an insoluble resinous residue.

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